A Novel Reaction of CS_2 with Organocopper(I) Complexes. Synthesis and Structure of {Tetra[μ-bis(diphenylphosphino)methane]di-μ_4-trithiocarbonato}tetracopper(I)–Toluene

Anna Maria Manotti Lanfredi,[a] Antonio Tiripicchio,[a] Annamaria Camus,[b] and Nazario Marsich[b]

[a] *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy*

[b] *Istituto di Chimica, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy*

The reaction of some arylcopper(I) complexes with carbon disulphide and bis(diphenylphosphino)methane (dppm), in toluene, affords the trithiocarbonato complex $[Cu_4(dppm)_4(CS_3)_2]$, whose structure, as the toluene solvate, was shown by *X*-ray analysis to consist of a square arrangement of copper atoms with the dppm ligands bridging the edges; each of the two trithiocarbonate anions is bonded to all the four copper atoms through two sulphur atoms only.

The reactions of carbon disulphide with transition metal complexes have been extensively investigated,[1] and owing to the high versatility of this reagent several types of products with various bonding modes to metals have been obtained. An unusual example of its reactivity with arylcopper(I) complexes (Ar = *o*-, *m*-, *p*-tolyl), in the presence of bis(diphenylphosphino)methane (dppm), is now reported. All three organocopper complexes with dppm: ArCu $\geqslant$ 1, gave the same product (**1**), together with the $[ArCS_2Cu(dppm)]_2$ complexes[2] obtained by the normal insertion of carbon disulphide into the copper–carbon bond.[3] *X*-Ray analysis has revealed that (**1**) is tetranuclear with the copper atoms bridged by both dppm ligands and CS_3^{2-} anions, formed from the condensation of two CS_2 molecules on elimination of CS.

$$[Cu_4(dppm)_4(CS_3)_2]$$

(**1**)

Although the tendency of CS_2 to form trithiocarbonate is already known,[4] (**1**) is the first crystallographically confirmed example of CS_3^{2-} anions nearly symmetrically bonded to four metal atoms, through two sulphur atoms only. Furthermore the known trithiocarbonate derivatives of copper(I) are very few, being limited to the mononuclear complexes Cu(S_2CSR)-

$(PPh_3)_2$,[5] some mixed ammonium or alkali metals salts,[6] and two anionic compounds $L(CuCS_3)$ (L = tetraphenylarsonium and -phosphonium).[7]

Complex (1) was obtained by adding dppm to toluene–CS_2 solutions of the organocopper complexes. The reactions were performed under an inert atmosphere, using dried, freshly redistilled solvents. A representative preparation is as follows: 5 ml of CS_2 were slowly added to a stirred suspension of *m*-tolylcopper[8] (0.9 g, 5.8 mmol) in toluene (30 ml) at 0 °C. After 10 min dppm (2.35 g, 7.0 mmol) was added to the red-brown solution formed, which was then allowed to reach room temperature. The colour turned green-brown and orange microcrystals precipitated on standing. They were filtered off, washed repeatedly with diethyl ether and dried *in vacuo*. Recrystallization from toluene–diethyl ether gave red-brown needles, m.p. 140—142 °C, with effervescence. Satisfactory elemental analytical data were obtained for $Cu_4(dppm)_4(CS_3)_2\cdot$ toluene.

Once the structure of (1) was established, we prepared (1) by another method: 2.0 ml (about 4.0 mmol) of a K_2CS_3 solution[9] were added to a solution of CuCl (0.5 g, 5.0 mmol) and dppm (2.0 g, 5.2 mmol) in deaerated dimethylformamide (30 ml). The orange precipitate, formed immediately, was dissolved in CS_2 and reprecipitated with MeOH, giving a microcrystalline, red-orange powder. On recrystallization from hot toluene–MeOH a product was obtained which was identical with that from the previous method (yield 80% with respect to dppm). This preparation seems specific for dppm, as similar complexes were not obtained with triphenylphosphine or 1,2-bis(diphenylphosphino)ethane.

The i.r. spectrum of (1) shows absorptions associated with the CS_3^{2-} groups at 925(s) and 835(s) cm^{-1}, the first at a somewhat lower value than those found for other known trithiocarbonate derivatives with dihapto co-ordinated CS_3^{2-} groups.[4,10] The ^1H n.m.r. spectrum (CS_2) shows the correct aromatic:methylene proton ratio. The aromatic protons are unresolved and give a multishoulder peak, centred at δ 6.8. The methylene protons also give a broad absorption peak at *ca.* δ 3.15 (δ 2.6 in the free ligand), indicating a strong interaction between phosphorus and adjacent copper atoms, similar to that observed between P and O for the $dppmO_2$ compound (δ 3.3). The ^{31}P n.m.r. spectrum shows a unique absorption at *ca.* δ −9 p.p.m. with respect to an external standard of 10% H_3PO_4 in D_2O (free ligand δ −22.7 p.p.m.).

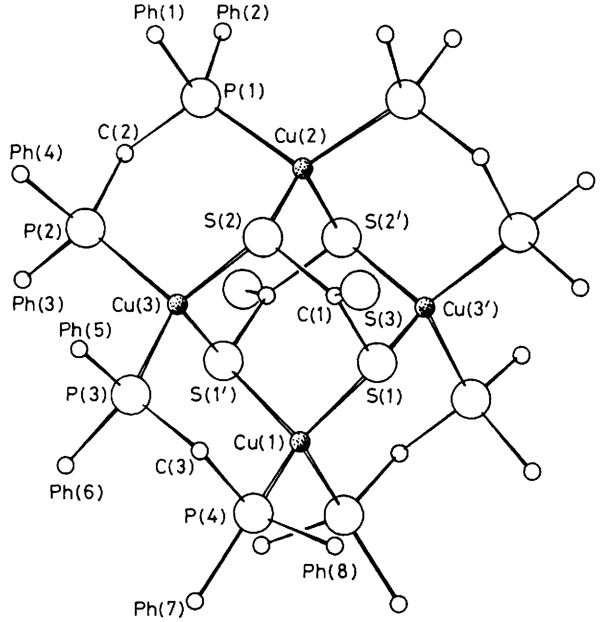

Figure 1. A view of complex (1) $[Cu_4(dppm)_4(CS_3)_2]$. Important bond distances (Å) and angles (°): Cu(1)–S(1) 2.406(7), Cu(3)–S(1′) 2.344(7), Cu(2)–S(2) 2.327(8), Cu(3)–S(2) 2.308(7), Cu(1)–P(4) 2.347(8), Cu(2)–P(1) 2.272(7), Cu(3)–P(2) 2.286(7), Cu(3)–P(3) 2.277(8), C(1)–S(1) 1.74(2), C(1)–S(2) 1.75(2), C(1)–S(3) 1.67(2); S(1)–Cu(1)–S(1′) 108.2(3), S(2)–Cu(2)–S(2′) 116.9(3), S(2)–Cu(3)–S(1′) 117.2(2), S(1)–C(1)–S(2) 122(1), S(1)–C(1)–S(3) 120(1), S(2)–C(1)–S(3) 118(1).

The structure of complex (1) $[Cu_4(dppm)_4(CS_3)_2]$ is shown in Figure 1 together with the more significant bond distances and angles.† The complex has an imposed crystallographic C_2 symmetry with the two-fold axis passing through the Cu(1) and Cu(2) atoms. The four copper atoms are in a square arrangement in which the Cu(1)–Cu(3) and Cu(2)–Cu(3) distances are 3.305(6) and 3.32(6) Å, respectively. Each edge is doubly bridged by a dppm ligand and a sulphur atom from a CS_3^{2-} anion. In both the trithiocarbonate anions two sulphur atoms only [S(1) and S(2)] are involved in co-ordination to the metal atoms and act as nearly symmetrical bridges between two copper atoms. This bonding mode of the CS_3^{2-} ion is uncommon; in the few studies characterizing the trithiocarbonate complexes, this ligand is bidentate either chelating to a metal to form a four-membered planar ring system CS_2M[5,11,12] or bridging two metal atoms.[13] η^3-Co-ordination has been found in the complex $[MoO(S_2CSR)_2]$ ($R = Pr^i$)[14] and spectroscopic data suggests behaviour as a tridentate (chelating and bridging) ligand in some metal complexes.[10]

Complex (1) reacts with dilute HCl releasing H_2S and giving CuCl(dppm). It also reacts immediately with MeI at room temperature giving CuI(dppm) together with other sulphurated products among which is the dimethyl ester of trithiocarbonic acid. A slower reaction is observed with dichloroethane, which releases CS_2, giving CuCl(dppm) and very small amounts of 1,3-dithiolane-2-thione. All these reaction products were identified by comparison of their i.r. spectra with those of pure samples.

In agreement with the established structure, complex (1) was obtained in high yield from the tetrameric *m*-[15] and *p*-tolylcopper[16] complexes, but in low yield from the *o*-tolylcopper derivative, which in aromatic hydrocarbons gives a hexanuclear species initially and only slowly equilibrates with a tetrameric form.[16] Furthermore, (1) was not obtained from the phenylcopper derivative, which has a higher degree of polymerization,[17] and prefers trimeric reactive groups.[3b,18] Similarly, only very small amounts of (1) were isolated from

---

† *Crystal data:* $C_{102}H_{88}Cu_4P_8S_6\cdot C_6H_5CH_3$, $M = 2100.29$, monoclinic, space group $C2/c$, $a = 21.356(5)$, $b = 20.033(6)$, $c = 26.989(7)$ Å, $\beta = 96.45(2)°$, $U = 11473(5)$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}, $F(000) = 4328$, $\mu(Cu\text{-}K_\alpha) = 32.19$ cm^{-1}. The intensities of 8501 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—60°); Ni-filtered Cu-K_α radiation and the θ–2θ scan technique were used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 3314 observed reflections [having $I \geqslant 2\sigma(I)$] to an R value of 8.5%. The toluene molecule lies on the centre of symmetry, and the methyl group, distributed over six equivalent positions, was not localised.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as Supplementary Publication No. SUP 23720 (21 pp) from the British Library Lending Division. For details of how to obtain this material, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983 Issue 3, p. xvii.

the mother liquors of the reaction between CS_2 and the trinuclear complex $Cu(dppm)_3 \cdot 2S$ (S = solvent).[19]

Received, 20th June 1983; Com. 811

References

1 I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161; P. V. Yaneff, *Coord. Chem. Rev.*, 1977, **23**, 183; I. S. Butler, *Acc. Chem. Res.*, 1977, **10**, 357; D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.

2 A. Camus, N. Marsich, and G. Pellizer, to be published.

3 (a) A. Miyashita and A. Yamamoto, *J. Organomet. Chem.*, 1976, **113**, 187; (b) A. Camus, N. Marsich, and G. Nardin, *ibid.*, 1980, **188**, 389.

4 D. H. M. W. Thewissen, *J. Organomet. Chem.*, 1980, **188**, 211; G. Thiele, G. Liehr, and E. Lindner, *ibid.*, 1974, **70**, 427.

5 P. G. Eller and R. R. Ryan, *Acta Crystallogr., Sect. B*, 1977, **33**, 619 and references therein.

6 G. Gattow and C. W. Voigt, *Z. Anorg. Allg. Chem.*, 1974, **409**, 185.

7 A. Müller, P. Christophliemk, I. Tossidis, and C. K. Jörgensen, *Z. Anorg. Allg. Chem.*, 1973, **401**, 274.

8 A. Camus and N. Marsich, *J. Organomet. Chem.*, 1968, **14**, 441.

9 J. P. Fackler and D. Coucouvanis, *J. Am. Chem. Soc.*, 1966, **88**, 3913.

10 C. Bianchini, C. Mealli, A. Meli, and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1982, 799.

11 A. Chiesi Villa, A. Gaetani Manfredotti, M. Nardelli, and C. Pelizzi, *J. Chem. Soc., Chem. Commun.*, 1970, 1322.

12 J. P. Fackler, Jr., and W. J. Zegarski, *J. Am. Chem. Soc.*, 1973, **95**, 8566.

13 D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, 1969, **91**, 761.

14 J. Hyde, K. Venkatasubramanian, and J. Zubieta, *Inorg. Chem.*, 1978, **17**, 414.

15 H. K. Hofstee, J. Boersma, and G. J. M. van Der Kerk, *J. Organomet. Chem.*, 1979, **168**, 241.

16 G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Org. Chem.*, 1977, **42**, 2047.

17 H. K. Hofstee, J. Boersma, and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1978, **144**, 255.

18 G. Costa, A. Camus, N. Marsich, and L. Gatti, *J. Organomet. Chem.*, 1967, **8**, 339.

19 A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Organomet. Chem.*, 1973, **60**, C39.